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A TECHNIQUE FOR STUDYING THE EXCHANGE OF
TRACE ELEMENTS BETWEEN ESTUARINE SEDIMENTS
AND WATER

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A TECHNIQUE FOR STUDYING THE EXCHANGE OF TRACE ELEMENTS BETWEEN ESTUARINE SEDIMENTS AND WATER¹

Trace elements are continuously exchanged between sediments and water in the estuarine environment. This exchange is an important part of the biogeochemical cycling of these elements and often determines their availability to the biota. Sediments usually contain large concentrations of trace elements relative to the water and serve as a reservoir for the elements. Radioisotopes have been used experimentally to study the sediment-water exchange of phosphate (Pomeroy, Smith, and Grant 1965), zinc (O'Connor and Renn 1964; Johnson, Cutshall, and Osterberg 1966; Bachmann 1963; Sonnen 1965), and other elements (Carritt and Goodgal 1954).

In this paper we describe a technique and specialized equipment for studying the exchange of elements between sediments and water. Exchange rates of zinc are determined for a series of sediment samples from the Newport River estuary at Beaufort, North Carolina.

MATERIALS AND METHODS

Natural cores of estuarine sediments are collected with a coring device constructed with a polyethylene cylinder that is plugged with a vinyl stopper and detached after a core is taken (Fig. 1). The cylinders are then transported to the laboratory and submerged in water from the sampling station in a 30-gallon (0.11 m³) plastic container. The water, circulated by aeration, is maintained at $22 \pm 2^\circ\text{C}$ and the pH and salinity are recorded. The sediment is left in contact with the water until the concentration of the trace element of interest becomes constant in the water. In the present experiments, zinc was analyzed periodically as reported by Duke, Willis, and Price (1966) until the difference between two consecutive measurements was less than 5% of the total concentration.

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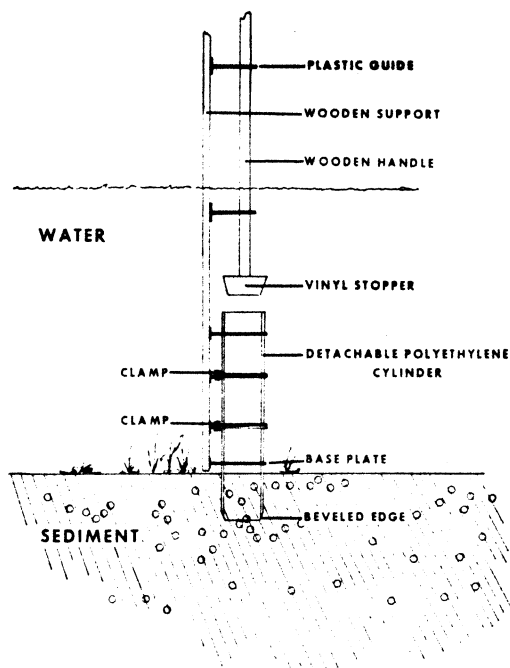


FIG. 1. Corer for taking sample of sediment and overlying water.

After this equilibrium is reached, the cylinders containing the cores and about 800 ml of water are removed from the plastic can. The water is pumped from the cylinder and filtered through a $0.45\text{-}\mu$ membrane filter. The inside of the cylinder is wiped clean, about 600 ml of the filtered water are returned to the cylinder, and the remainder is used for chemical analysis. These operations must be completed carefully to avoid disturbance of the sediment surface.

After the filtered water is in place over the core, the cylinders are slipped into a specially constructed lead shield (Fig. 2). The shield consists of three parts arranged so that a 2-inch (5.4 cm) sodium iodide crystal detects only the radiation passing through a narrow slit (1.6 cm high) focused on a limited portion of the sample cylinder. The detector is hooked to a rate meter and 10-mv recorder. The radioactivity from a

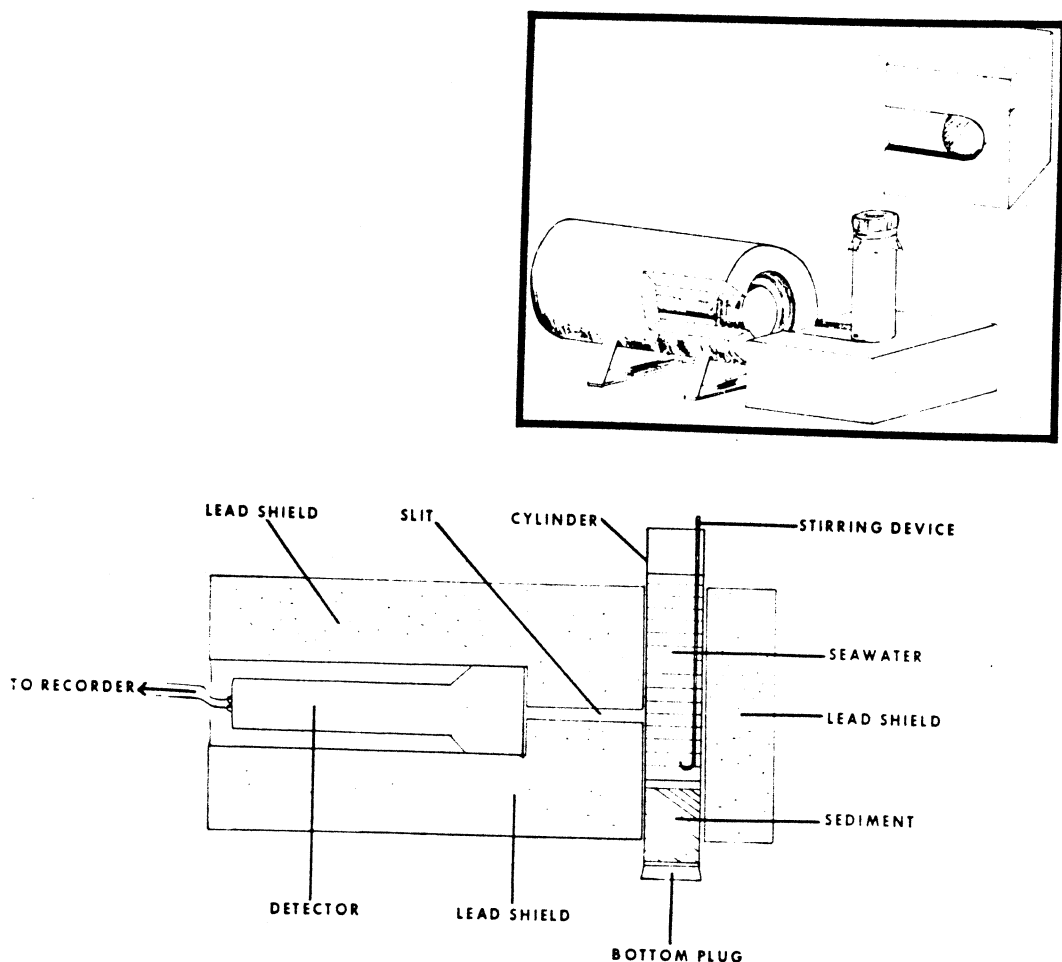


FIG. 2. Apparatus for measuring loss of radionuclide from water to sediment instantaneously and continuously.

narrow wedge of the water column can thus be measured and recorded both instantaneously and continuously.

Carrier-free radioactive tracer is added to the column of water through a plastic pipette positioned so that the tracer is released 8 cm below the surface and in the center of the water column. A J-shaped plastic aeration tube is attached to the inside wall of the cylinder and extends to the midpoint of the water column. Filtered compressed air is pumped through the tube at a rate that does not disturb the sediment surface but does ensure circulation and mixing of water above the sediment. Preliminary studies showed that

when the cylinder is in position, radiation from the sediment cannot be detected. Thus, only loss of the tracer from the water is recorded. A blank cylinder containing only filtered water is spiked with tracer and analyzed so that a curve representing movement of the tracer due to processes other than exchange with the sediment can be determined. During the analysis, the top of the cylinder is covered with Saran Wrap to ensure that radioactivity is not lost in the spray from bursting air bubbles.

In the exchange of any element between water and sediments, at equilibrium, when the concentration of the traced element in the water remains constant, the rate of

movement of the element from water to sediment equals the rate of movement from sediment to water. Thus

$$\begin{aligned}\rho w \rightarrow s &= \rho s \rightarrow w \\ &= \rho \text{ (the overall rate of exchange).}\end{aligned}$$

Or written in the notation of compartmental analysis (Sheppard 1962), for the general case of n water compartments and m sediment compartments

$$\begin{aligned}&(\rho w_1 \rightarrow s_1 + \rho w_1 \rightarrow s_2 \dots + \rho w_1 \rightarrow s_m) \\ &+ (\rho w_2 \rightarrow s_1 + \rho w_2 \rightarrow s_2 \dots + \rho w_2 \rightarrow s_m) \\ &\dots \dots \dots \\ &+ (\rho w_n \rightarrow s_1 + \rho w_n \rightarrow s_2 \dots + \rho w_n \rightarrow s_m) \\ &= (\rho s_1 \rightarrow w_1 + \rho s_1 \rightarrow w_2 \dots + \rho s_1 \rightarrow w_n) \\ &\quad + (\rho s_2 \rightarrow w_1 + \rho s_2 \rightarrow w_2 \dots + \rho s_2 \rightarrow w_n) \\ &\quad \dots \dots \dots \\ &\quad + (\rho s_m \rightarrow w_1 + \rho s_m \rightarrow w_2 \dots + \rho s_m \rightarrow w_n),\end{aligned}$$

where $\rho 1 \rightarrow 2$ = rate of movement of traced substance from compartment 1 to compartment 2; w = water; s = sediment; and t = time. In later equations (below), S_1 = amount of traced substance in compartment 1; R_1 = absolute amount of tracer in compartment 1; and a_1 = specific activity of compartment 1. If a tracer is introduced into the water, its movement from the water can be described:

$$\begin{aligned}dR_w/dt &= \text{--rate of movement of tracer} \\ &\quad \text{from water to sediment} \\ &\quad + \text{rate of return of tracer} \\ &\quad \text{from sediment to water.}\end{aligned}$$

At any instant the rate of movement of tracer from water to sediment equals the rate of movement of traced substance from water to sediment times the fraction labeled = $\rho \times a_w$, and similarly the rate of movement of tracer from sediment to water = $\rho \times a_s$, or $dR_w/dt = -\rho \times a_w + \rho \times a_s$. Since many compartments may be present in the sediment

$$\begin{aligned}dR_w/dt &= -[(\rho w_1 \rightarrow s_1 \times a_{w_1} + \rho w_1 \rightarrow s_2 \times a_{w_1} \\ &\quad \dots + \rho w_1 \rightarrow s_m \times a_{w_1}) \\ &\quad + (\rho w_2 \rightarrow s_1 \times a_{w_2} + \rho w_2 \rightarrow s_2 \times a_{w_2} \\ &\quad \dots + \rho w_2 \rightarrow s_m \times a_{w_2}) \dots \\ &\quad + (\rho w_n \rightarrow s_1 \times a_{w_n} + \rho w_n \rightarrow s_2 \times a_{w_n} \\ &\quad \dots + \rho w_n \rightarrow s_m \times a_{w_n})]\end{aligned}$$

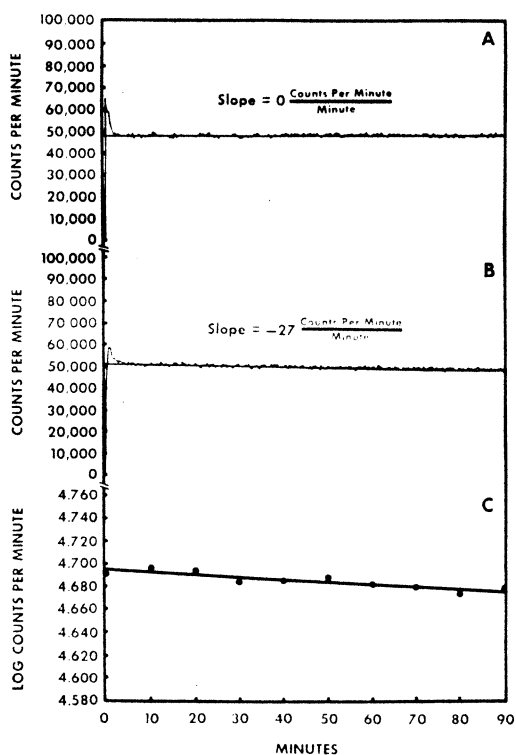


Fig. 3. Rates of movement of ^{65}Zn from water to sediments and walls of plastic cylinders. Graph A represents movement of ^{65}Zn in control cylinder; B represents movement of ^{65}Zn from water to sediment in typical sample from Newport River, North Carolina; and C shows a plot of log concentration of ^{65}Zn in the water vs. time to be a straight line for first 90 min.

$$\begin{aligned}&+ [(\rho s_1 \rightarrow w_1 \times a_{s_1} + \rho s_1 \rightarrow w_2 \times a_{s_1} \\ &\quad \dots + \rho s_1 \rightarrow w_n \times a_{s_1}) \\ &\quad + (\rho s_2 \rightarrow w_1 \times a_{s_2} + \rho s_2 \rightarrow w_2 \times a_{s_2} \\ &\quad \dots + \rho s_2 \rightarrow w_n \times a_{s_2}) \dots \\ &\quad + (\rho s_m \rightarrow w_1 \times a_{s_m} + \rho s_m \rightarrow w_2 \times a_{s_m} \\ &\quad \dots + \rho s_m \rightarrow w_n \times a_{s_m})].\end{aligned}$$

However, for determining the overall exchange rate across the sediment-water interface, it should be possible to describe the water-sediment exchange system by equations for only two exchanging compartments, water and sediment, during a short interval after the introduction of tracer (principle of lumping), giving:

$$dR_w/dt \cong \rho \times (a_s - a_w),$$

and near $t = 0$, $a_s \cong 0$. Therefore,

$$dR_w/dt \cong -\rho \times a_w,$$

and since

$$a_w = R_w/S_w,$$

$$dR_w/dt \cong -\rho \times R_w/S_w,$$

and

$$dR_w/R_w \cong -(\rho/S_w) dt.$$

Assuming ρ and S_w constant and integrating over limits $R = R_{w_0}$, $t = 0$ to $R = R_w$, $t = t$, then

$$\ln R_w \cong \ln R_{w_0} - (\rho/S_w) t,$$

$$2.303 \log R_w \cong 2.303 \log R_{w_0} - (\rho/S_w) t,$$

and

$$\log R_w \cong \log R_{w_0} - (\rho/2.303 S_w) t.$$

Therefore, lumping of the water and sediment compartments into only two compartments and assuming that $a_s = 0$ is permissible, as long as a plot of $\log R_w$ vs. t gives a straight line. This is shown to be true for the first 90 min in Fig. 3.

Now since $dR_w/dt \cong -\rho \times a_w$ during the first 90 min, then, near $t = 0$,

$$\rho = - \frac{dR_w/dt}{a_w}.$$

The rate, dR_w/dt is assumed to be equal to the slope of the R_w vs. t plot which is calculated by inspection from the first 35 min of the curve after the elimination of the first 5 min during which mixing occurred. This assumption is permissible since the slope is essentially constant over the first 35 min after the addition of tracer (Fig. 3). The rate of exchange, ρ , is then computed from the values of dR_w/dt and that calculated for a_w at $t = 0$.

ρ is the rate of exchange of the substance between the water and sediment actually contained in the experimental cylinders. To make this rate applicable to the estuary, the rate is divided by the exposed surface area of the sediment contained in the cylinder, giving

$$\frac{\rho w \rightleftharpoons s}{m^2} = - \frac{dR_w/dt}{a_w \text{ (surface area of sediment)}}$$

The exchangeable amount of element in the sediment can be determined from the specific activity in the water after the tracer has equilibrated with the sediments. After the cylinders are analyzed for 2 hr for the loss of the tracer, they can be removed from the shield, stored with aerating device in place, then periodically replaced in the shield and analyzed for tracer content. At equilibrium, that is, when there is no further loss of isotope from the water, the amount of exchangeable element in the sediment can be calculated from the expressions:

Specific activity of water = Specific activity of sediment;

$$\begin{aligned} R_w/S_w &= R_s/S_s; \\ S_s &= R_s S_w / R_w. \end{aligned}$$

APPLICATION OF TECHNIQUE

Cores collected in June 1967 from the mouth of the Newport River estuary in Beaufort, N.C., were analyzed for rate of zinc exchange by this technique. Cores consisted of 32% sand (>0.05 mm), 38% coarser silt ($0.05-0.025$ mm), 18% coarse silt ($0.025-0.005$ mm), 2% fine silt ($0.005-0.002$ mm), and 10% total clay (<0.002 mm). Carrier-free ^{65}Zn as $^{65}\text{ZnCl}_2$ was used as the tracer. Exchange rates were calculated as described above, assuming that the tracer mixed immediately and completely with the exchangeable zinc in the water and that the stable zinc concentration in the water was constant during the 30-min period in which loss of the tracer was observed. The average rate of exchange for 10 cores was $17 \pm 4 \mu\text{g of Zn hr}^{-1} \text{ m}^{-2}$. This technique is applicable to studies of any other element with a convenient gamma-emitting isotope, as long as no isotopic effects occur.

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REFERENCES

- BACHMANN, R. W. 1963. Zinc-65 in studies of the freshwater zinc cycle, p. 485-496. In V. Schultz and A. W. Klement, Jr. [eds.], *Radioecology*. Reinhold Publ., New York, and *Am. Inst. Biol. Sci.*, Washington, D.C.
- CARRITT, D. E., AND S. GOODGAL. 1954. Sorption reactions and some ecological implications. *Deep-Sea Res.*, 1: 224-243.
- DUKE, T. W., J. N. WILLIS, AND T. J. PRICE. 1966. Cycling of trace elements in the estuarine environment. I. Movement and distribution of zinc 65 and stable zinc in experimental ponds. *Chesapeake Sci.*, 7: 1-10.
- JOHNSON, V., N. CUTSHALL, AND C. OSTERBERG. 1967. Retention of ^{65}Zn by Columbia River sediment. *Water Resources Res.*, 3: 99-102.
- O'CONNOR, J. T., AND C. E. RENN. 1964. Soluble-absorbed zinc equilibrium in natural waters. *J. Am. Water Works Assoc.*, 56: 1055-1061.
- POMEROY, L. R., E. E. SMITH, AND C. M. GRANT. 1965. The exchange of phosphate between estuarine water and sediments. *Limnol. Oceanog.*, 10: 167-172.
- SHEPPARD, C. W. 1962. Basic principles of the tracer method. Wiley, New York. 282 p.
- SONNEN, M. B. 1965. Zinc adsorption by sediments in a saline environment. *Univ. Ill., Civil Engr. Studies*, Ser. 24, COO-1264-1. 42 p.